JOC Article

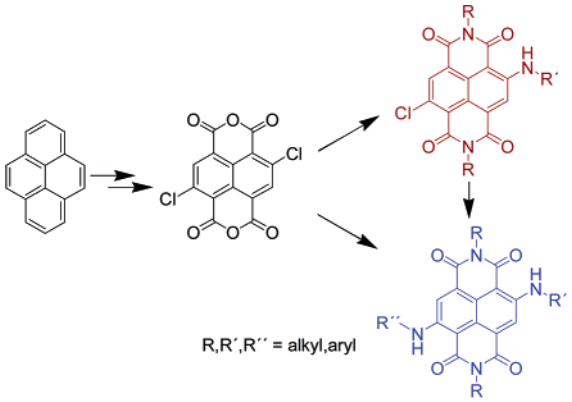
Synthesis and Optical and Redox Properties of Core-Substituted Naphthalene Diimide Dyes

Christoph Thalacker, Cornelia Röger, and Frank Würthner*

Universität Würzburg, Institut für Organische Chemie, Am Hubland, 97074 Würzburg, Germany

wuerthner@chemie.uni-wuerzburg.de

Received June 14, 2006



2,6-Dichloronaphthalene dianhydride has been synthesized by a modified procedure. The imidization of this dichlorinated anhydride with amines and subsequent stepwise nucleophilic exchange of the chlorine atoms by alkyl- or arylamines afforded a series of hitherto unknown monoamino- and diamino-substituted naphthalene diimides. An alternative route for the synthesis of diamino-substituted naphthalene diimides is also reported. Optical and electrochemical properties of the newly synthesized amino-functionalized naphthalene diimides were studied in detail. The absorption maxima (530−620 nm) of these dyes are appreciably bathochromically shifted compared to those of the corresponding core-unsubstituted compounds. At the naphthalene core alkylamino-substituted diimides exhibit fluorescence quantum yields up to 60%.

Introduction

The higher homologues of 1,4,5,8-naphthalenetetracarboxylic acid diimide (NDI, this class of compounds is also called as naphthalene bisimide), namely perylene,[1] terrylene,[2] and quaterrylene[3] diimides, are well-established fluorescent colorants with outstanding lightfastness, chemical inertness, and high fluorescence quantum yields. Their outstanding optical properties can be ascribed to the extended aromatic π system. While core-unsubstituted NDIs show absorption only in the UV region,[4] core-unsubstituted perylene diimides with larger π system are red dyes with absorption maxima (λ_{max}) at around 530 nm and fluorescence emission (λ_{em}) bands in the range of 500−560 nm.[1c,5] With one more naphthalene unit extended terrylene diimides are blue colorants ($\lambda_{max} \approx 650$ nm), and they show fluorescence around 670 nm,[2] while quaterrylene diimides exhibit absorption ($\lambda_{max} \approx 760$ nm) and fluorescence maxima

* To whom correspondence should be addressed. Tel: + 49 (0)931-8885340. Fax: + 49-(0)931-8884756.

(1) (a) Zollinger, H. *Color Chemistry*, 2nd ed.; VCH: Weinheim, 1991. (b) Herbst, W.; Hunger, K. *Industrial Organic Pigments, Production, Properties, Applications*; Wiley-VCH: Weinheim, 1997. (c) Langhals, H. *Heterocycles* **1995**, *40*, 477−500. (d) Würthner, F. *Chem. Commun.* **2004**, 1564−1579.

(2) (a) Holtrup, F. O.; Müller, G. R. J.; Quante, H.; De Feyter, S.; De Schryver, F. C.; Müllen, K. *Chem. Eur. J.* **1997**, *3*, 219−225. (b) Mais, S.; Tittel, J.; Basché, T.; Bräuchle, C.; Göhde, W.; Fuchs, H.; Müller, G.; Müllen, K. *J. Phys. Chem. A* **1997**, *101*, 8435−8440.

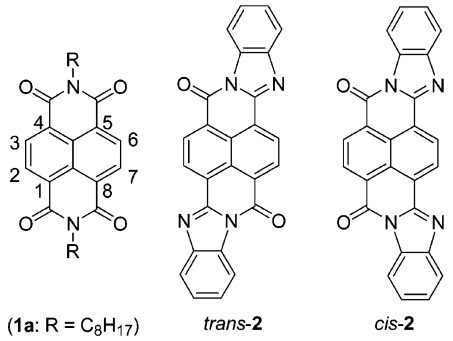
(3) (a) Quante, H.; Müllen, K. *Angew. Chem.* **1995**, *107*, 1487−1489; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1323−1325. (b) Geerts, Y.; Quante, H.; Platz, H.; Mahrt, R.; Hopmeier, M.; Böhm, A.; Müllen, K. *J. Mater. Chem.* **1998**, *8*, 2357−2369. (c) Könemann, M.; Böhm, A.; Bidlingmaier, H.; Rieger, R.; Blaschka, P.; Reichelt, H.; Krieger, M. (BASF AG), German Pat. DE 102004041604A1, 2006. (d) Pschirer, N. G.; Kohl, C.; Nolde, F.; Qu, J.; Müllen, K. *Angew. Chem.* **2006**, *118*, 1429−1432.

(4) (a) Alp, S.; Erten, U.; Karapire, C.; Köz, B.; Doroshenko, A. O.; Içli, S. *J. Photochem. Photobiol. A* **2000**, *135*, 103−110. (b) Licchelli, M.; Biroli, A. O.; Poggi, A. *Org. Lett.* **2006**, *8*, 915−918.

(5) Würthner, F.; Chen, Z.; Dehm, V.; Stepanenko, V. *Chem. Commun.* **2006**, 1188−1190.

10.1021/jo0612269 CCC: $33.50
Published on Web 09/19/2006

CHART 1. Structures of NDIs 1 and "Perinone" Pigments 2[a]



[a] In the solid state, the trans isomer of **2** is orange and the cis isomer is red.

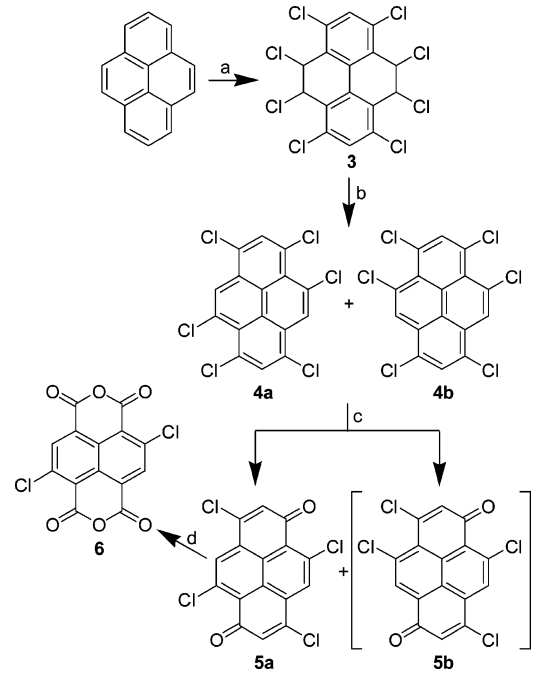
($\lambda_{em} \approx 780$ nm) approaching the near-infrared region.[3] Due to the lack of absorption in the visible range for core-unsubstituted NDIs, technical application of NDI-based colorants has been restricted to derivatives with extended aromatic systems such as "perinones" (Chart 1); the latter can be obtained by condensation of naphthalene dianhydride with *o*-phenylenediamine and have been used as vat dyes since the 1930s and as pigments since the 1950s.[1a,b]

NDIs with bathochromically shifted absorption maxima can be achieved by functionalization at the naphthalene core.[6] Recently, we have shown that attachment of electron-donating alkylamino and alkyloxy substituents at the 2,6-positions of NDI **1** (Chart 1) can even afford valuable fluorophores with fluorescence quantum yields up to 80% and tunable emission wavelengths from the green to red spectral region.[7] In this work, we present a broader range of new NDIs bearing different amino substituents at the naphthalene core. The effect of alkylamino and arylamino substituents on the optical and redox properties of NDIs has been studied in detail to elicit a structure−property relationship. Furthermore, a new route to core-substituted NDI is introduced.

Results and Discussion

Synthesis. Vollmann's synthesis[6a] of core-substituted NDIs starts with naphthalene dianhydride **6** (Scheme 1). The latter can be obtained in four steps from pyrene by subsequent chlorination, HCl elimination, and oxidation.[6a] However, the procedure reported in this classical publication[6a] could not be reproduced in a satisfying manner. Modification of this procedure resulted in successful synthesis of **6**, which we describe in detail in the Experimental Section. In the course of chlorination of pyrene (Scheme 1, reaction a), it is essential to adjust the reaction temperature in particular time intervals. The separation of 2,6- and 2,7-dichloro isomers was achieved at the quinone stage where the 2,6 isomer **5a** precipitated from the

SCHEME 1. Synthesis of Regioisomerically Pure Naphthalene Dianhydride 6[a]



[a] Reagents and conditions: (a) Cl_2 (g), I_2 (in catalytic amounts), 1,2,4-trichlorobenzene, 25−110 °C, 6 h, yield 36−38% of **3**; (b) KOH, ethanol, 80 °C, 5 h, yield 96−97% of **4a**,**b** as an isomeric mixture; (c) fuming HNO_3, 0−5 °C, 15 min, yield 32−45% of **5a** (isomer **5b** was not purified); (d) fuming HNO_3, concd H_2SO_4, 100 °C, 5 min, yield 45−49% of **6**.

reaction mixture. For this reaction, we used fuming nitric acid, instead of concentrated nitric acid as used in the previously reported procedure. The trans isomer **5a** was separated by filtration, and purification could be achieved by sublimation. The ^{1}H NMR spectrum of **5a** in deuterated concentrated sulfuric acid showed only two signals at 7.96 and 6.76 ppm, which can be taken as an evidence for the isolated trans product.

Reaction of **6** with primary aliphatic or aromatic amines in refluxing glacial acetic acid yielded the corresponding 2,6-dichloro-substituted NDIs **7a**,**b** (Scheme 2). In this highly protic solvent, where most amino functions are protonated, the reactivity of the amines is sufficiently low; thus, imide formation is more favored over substitution of the chlorine atoms. Only for an elongated reaction time did nucleophilic aromatic substitution (S_NAr) take place to a small extent.

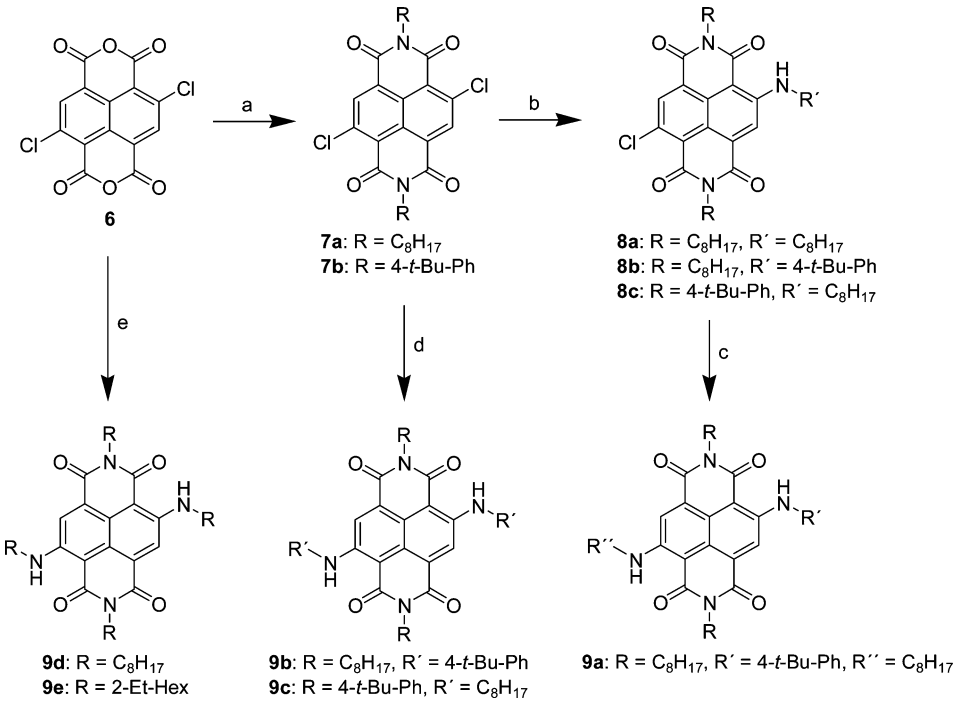
Reaction of dichlorinated NDIs **7a**,**b** with *n*-octylamine at room temperature in aprotic organic solvents, such as dichloromethane, leads to selective substitution of one chlorine atom to afford the corresponding monochloroalkylaminonaphthalene diimides **8a**,**c**. This convincingly demonstrates the high propensity of these electron-deficient aromatic compounds toward nucleophilic substitution, since amination of aryl halides usually requires either very harsh reaction conditions or transition metal catalysis.[8] Selective monosubstitution by less nucleophilic aromatic amines, e.g., 4-*tert*-butylaniline, was achieved in *N*-ethyldiisopropylamine at 140 °C. The resulting 2-chloro-6-arylaminonaphthalene diimide **8b** could be subjected to a second nucleophilic substitution with an alkylamine at 140 °C to yield the unsymmetrically substituted 2,6-diaminonaphthalene diimide **9a**.

NDIs **9b** and **9c** with two identical amino substituents were obtained directly by the reaction of 2,6-dichloro diimide **7a** or

(6) (a) Vollmann, H.; Becker, H.; Corell, M.; Streeck, H. *Liebigs Ann.* **1937**, *531*, 1−159. (b) Bonnet, E.; Gangneux, P.; Maréchal, E. *Bull. Soc. Chim. Fr.* **1976**, 504−506. (c) Bondarenko, E. F.; Shigalevskii, V. A.; Gerasimenko, Y. E. *Zh. Org. Khim.* **1979**, *15*, 2520−2525; *J. Org. Chem. USSR (Engl. Transl.)* **1979**, *15*, 2279−2284. (d) Bondarenko, E. F.; Shigalevskii, V. A.; Yugai, G. A. *Zh. Org. Khim.* **1982**, *18*, 610−615; *J. Org. Chem. USSR (Engl. Transl.)* **1982**, *18*, 530−535.

(7) Würthner, F.; Ahmed, S.; Thalacker, C.; Debaerdemaeker, T. *Chem. Eur. J.* **2002**, *8*, 4742−4750. For a recent application of these chromophores in artificial photosynthesis, see: Bhosale, S.; Sisson, A. L.; Talukdar, P.; Fürstenberg, A.; Banerji, N.; Vauthey, E.; Bollot, G.; Mareda, J.; Röger, C.; Würthner, F.; Sakai, N.; Matile, S. *Science* **2006**, *313*, 84−86.

SCHEME 2. Synthesis of Core-Substituted NDIs 7−9[a]



[a] Reagents and conditions: (a) Respective amine, glacial acetic acid, 120 °C, yield 70% of **7a** and 60% of **7b**; (b) **8a**,**c**: *n*-octylamine, CH_2Cl_2, 25 °C, 4.5−24 h, yield 96% of **8a** and 87% of **8c**; **8b** 4-*tert*-butylaniline, *N*-ethyldiisopropylamine, Ar, 140 °C, 1 h, yield 97% of **8b**; (c) *n*-octylamine, Ar, 140 °C, 45 min, yield 59% of **9a**; (d) respective amine, Ar, 140−180 °C, 40−60 min, yield 57% of **9b** and 43% of **9c**; (e) amine, Ar, 140 °C, 40−120 min, yield 70% of **9d** and 45% of **9e**.

7b, respectively, with an appropriate amine at 140 °C (alkylamine for **9c**) or at 180 °C (aromatic amine for **9b**). During the synthesis of **9c**, a partial exchange of the aromatic imide substituents for the alkylamine took place, owing to the large excess of alkylamine. Apparently, arylamines are easily replaced by alkylamines, while the inverse reaction was not observed during the synthesis of **9b**. The use of transition-metal-catalyzed reactions[8] for the introduction of the second amino function might be helpful to overcome this problem by employing milder reaction conditions under which an exchange of the imide substituents should be disfavored. Finally, NDIs **9d** and **9e** bearing the same substituents at both imide and core positions could be obtained in a one-step reaction from dianhydride **6** and the respective amines under heating at 140 °C (Scheme 2).

The synthesis of the precursor **6** for amino-functionalized NDIs **8**,**9** is rather cumbersome as depicted in Scheme 1. Therefore, we have been looking for an alternative route to aminonaphthalene diimides. In this regard, the functionalization of the readily available unsubstituted naphthalene dianhydride **10** appears to be promising. It was previously reported that naphthalene dianhydride **10** can be directly brominated with bromine in concentrated sulfuric acid.[9] However, this protocol could not be reproduced. Fortunately, the bromination of **10** was achieved using dibromoisocyanuric acid (DBI) in oleum (20% SO_3), which is known as one of the most powerful brominating agents (Scheme 3).[10] Application of a stoichiometric amount of DBI afforded a mixture consisting of mainly 2,6-dibromonaphthalene dianhydride **11** and small amounts of 2-monobromo and 2,3,6-tribromo compounds, along with some unreacted naphthalene dianhydride. The reaction of dibromonaphthalene dianhydride **11** with 2-ethylhexylamine at 140 °C afforded in a single step the 2,6-diamino-substituted NDI **9e** bearing identical substituents at the imide and core positions. Thus, a new route for the synthesis of symmetrically substituted diaminonaphthalene diimides with different substituents at the imide positions and naphthalene core may be synthesized from compound **9e** by hydrolysis of the latter to the corresponding diaminonaphthalene dianhydride and its subsequent imidization with different amines. Unfortunately, NDI **9e**, in contrast to structurally related perylene diimides,[11] could not be saponified to the corresponding dianhydride with KOH in alcohol. Instead, under these conditions lactam imide **12** was formed in good yield (Scheme 3, reaction c). Variation of reaction conditions (KOH/*t*-BuOH/water or KOH/18-crown-6/toluene) and prolonged reaction time (up to 48 h) did not lead to the formation of desired product. Rather, lactam imide **12** along with small

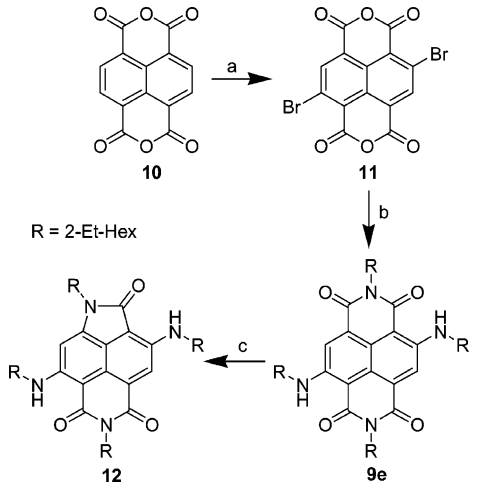
(8) Reviews on amination of aryl halides can be found in: (a) Wolfe, J. P.; Wagaw, S.; Marcoux, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805−818. (b) Hartwig, J. F. *Angew. Chem.* **1998**, *110*, 2154−2177; *Angew. Chem., Int. Ed.* **1998**, *37*, 2046−2067. Transition-metal-catalyzed amination of activated aryl halides at room temperature is described in: (c) Wolfe, J. P.; Buchwald, S. L. *Angew. Chem.* **1999**, *111*, 2570−2573; *Angew. Chem., Int. Ed.* **1999**, *38*, 2413−2416. (d) Stauffer, S. R.; Lee, S.; Stambuli, J. P.; Hauck, S. I.; Hartwig, J. F. *Org. Lett.* **2000**, *2*, 1423−1426. (e) Wolfe, J. P.; Tomori, H.; Sadighi, J. P.; Yin, J.; Buchwald, S. L. *J. Org. Chem.* **2000**, *65*, 1158−1174.

(9) (a) Solomatin, G. G.; Filippov, M. P.; Shigalevskii, V. A. *Zh. Org. Khim.* **1981**, *17*, 877−879; *J. Org. Chem. USSR (Engl. Transl.)* **1981**, *17*, 771−773. (b) Jacquignon, P.; Buu-Hoï, N. P.; Mangane, M. *Bull. Soc. Chim. Fr.* **1964**, 2517−2523.

(10) (a) Gottardi, W. *Monatsh. Chem.* **1968**, *99*, 815−822. (b) Gottardi, W. *Monatsh. Chem.* **1969**, *100*, 42−50. (c) Gottardi, W. *Monatsh. Chem.* **1977**, *108*, 1067−1084. (d) Becker, H. G. O., et al. *Organikum*, 19th ed.; Barth: Leipzig, 1993; pp 329−333.

(11) (a) Würthner, F.; Stepanenko, V.; Chen, Z.; Saha-Möller, C. R.; Kocher, N.; Stalke, D. *J. Org. Chem.* **2004**, *69*, 7933−7939. (b) Zhao, Y.; Wasielewski, M. R. *Tetrahedron Lett.* **1999**, *40*, 7047−7050. (c) Böhm, A.; Arms, H.; Henning, G. Blaschka, P. (BASF AG), German Pat. DE 19547209A1, 1997; *Chem. Abstr.* **1997**, *127*, 96569g.

SCHEME 3. Synthesis of 2,6-Diaminonaphthalene Diimide 9e by Functionalization of Naphthalene Dianhydride 10 in Two Steps[a]



[a] Reagents and conditions: (a) dibromoisocyanuric acid (DBI), oleum (20% SO_3), 25 °C, 5 h, yield 80% of **11**; (b) 2-ethylhexylamine, Ar, 140 °C, 2 h, yield 45% of **9e**; (c) KOH, *t*-BuOH, water, 80 °C, 24 h, yield 64% of **12**.

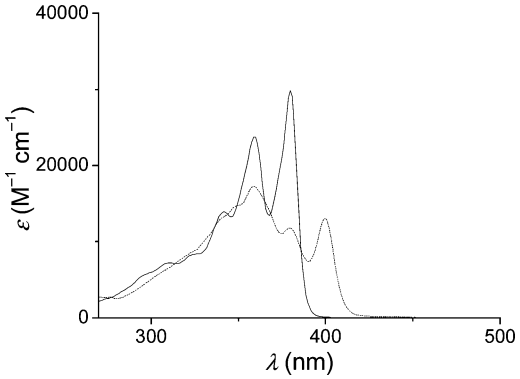


FIGURE 1. Absorption spectra of core-unsubstituted NDI **1a** (solid line) and 2,6-dichloronaphthalene diimide **7a** (dotted line) in dichloromethane.

amounts of unreacted NDI **9e** was isolated. It is noteworthy that such transformations have been reported earlier for other NDI derivatives[11e,12] and for some perylene diimides under special conditions as well.[13]

Optical Properties. The absorption spectra of core-unsubstituted NDIs **1** exhibit as major feature the electronic S_0-S_1 absorption band at 250−400 nm. The pronounced vibronic fine structure of the absorption band indicates the rigid nature of these chromophores and its energy in the order of ca. 1300 cm^{-1} (0.16 eV) corresponds to the skeletal vibrations of the aromatic system (Figure 1). While the higher homologue perylene diimides exhibit very strong fluorescence,[1,5] virtually no emission could be observed for unsubstituted NDIs **1**.[4] The S_0-S_1 band of the 2,6-dichloro-substituted NDIs **7a**,**b** is located at almost the same position as for NDIs **1**, but the vibronic fine

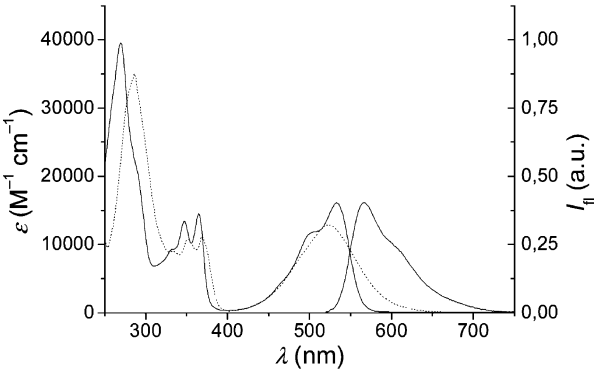
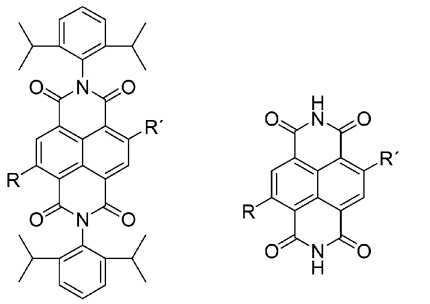


FIGURE 2. Absorption and emission spectra of **8c** (solid lines) and absorption spectrum of **8b** (dotted line) in dichloromethane. The excitation wavelength was 530 nm. The absorption and fluorescence spectra of **8a** are very similar to those of **8c**.

CHART 2. Structures of Previously Synthesized Disubstituted NDIs 13a,b[7] and 14a,b[14]



structure is quite different (Figure 1). The dichlorosubstituted NDIs **7a**,**b** are also not fluorescent. Upon introduction of amino substituents to the naphthalene core, significant changes in optical properties of NDIs were observed.[6,7,14,15] Thus, one amino substituent (compounds **8a**−**c** and **13a**, **14a** (Chart 2)) leads to red dyes with a new absorption band in the visible region at around 530 nm (Figure 2 and Table 1). For compounds bearing alkylamino groups (**8a**,**c**, **13a**, **14a**) at the naphthalene core, the S_0-S_1 band exhibits a shoulder at lower wavelengths. In aliphatic solvents this shoulder is more pronounced, and an additional shoulder occurs at even lower wavelengths. As the energy of the fine structure is again in the order of ca. 1300 cm^{-1} (0.16 eV), they can be attributed to a vibronic fine structure arising from the skeletal vibrations of the aromatic core. Interestingly, strong fluorescence bands were observed for the alkylamino-functionalized NDIs **8a**,**c**, which are mirror images of the S_0-S_1 absorption bands of these chromophores as exemplarily shown for **8c** in Figure 2. In contrast to alkylamino-substituted dyes **8a**,**c**, for the monoarylamino derivative **8b** neither fine vibronic structure nor fluorescence could be observed (Figure 2).

Introduction of a second electron-donating amino substituent at the naphthalene core evokes a further red shift of the new absorption band observed for the monoamino-substituted compounds to 610−620 nm providing the blue dyes **9a**−**e**, **13b**, and **14b** (Figure 3 and Table 1). As in the case of arylamino-

(12) (a) Bondarenko, E. F.; Shigalevskii, V. A. *Zh. Org. Khim.* **1986**, *22*, 1282−1286; *J. Org. Chem. USSR (Engl. Transl.)* **1986**, *22*, 1155−1163. (b) Langhals, H.; v. Unold, P. C. (Ciba Specialty Chemicals Corp.), US Pat. 5886183, 1999.

(13) Kaiser, H.; Lindner, J.; Langhals, H. *Chem. Ber.* **1991**, *124*, 529−535.

(14) Thalacker, C.; Miura, A.; De Feyter, S.; De Schryver, F. C.; Würthner, F. *Org. Biomol. Chem.* **2005**, *3*, 414−422.

(15) Thalacker, C. Ph.D. Thesis, Universität Ulm, 2001.

TABLE 1. Absorption Maxima (λ_{abs}), Absorption Coefficients (ϵ), Emission Maxima (λ_{em}), and Fluorescence Quantum Yields (Φ_{fl}) of Red NDI Dyes 8a−c, 13a, and 14a and Blue Dyes 9a−e, 13b, and 14b in Dichloromethane

	substituent		λ_{abs}	ϵ	λ_{em}	
compd	imide	core	(nm)	(M^{-1} cm^{-1})	(nm)	Φ_{fl}
8a	alkyl	NHalkyl	532	15 300	567	0.58
8b	alkyl	NHaryl	523	12 900	*a*	*a*
8c	aryl	NHalkyl	534	16 000	566	0.58
13a	aryl	NHalkyl	535	15 500	565	0.63
14a	H	NHalkyl	537[b]	16 200[b]	565[b]	0.57[b]
9a	alkyl	NHalkyl/aryl	613	22 200	*a*	*a*
9b	alkyl	NHaryl	612	22 800	*a*	*a*
9c	aryl	NHalkyl	618	23 600	650	0.55
9d	alkyl	NHalkyl	615	23 000	646	0.53
9e	alkyl	NHalkyl	619	22 100	647	0.53
13b	aryl	NHalkyl	620	23 300	650	0.42
14b	H	NHalkyl	620[b]	22 200[b]	648[b]	0.53[b]

[a] Not fluorescent. [b] Chloroform was used instead of dichloromethane for better solubility.

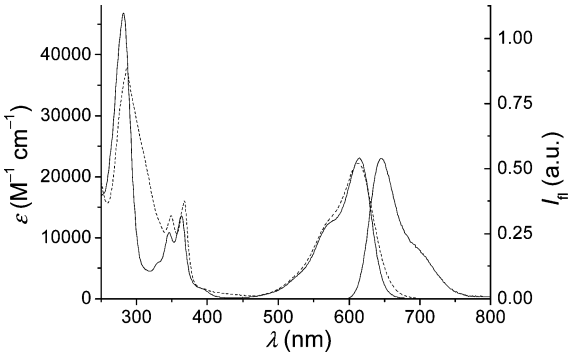


FIGURE 3. Absorption and emission spectra of **9d** (solid lines) and absorption spectrum of **9a** (dotted line) in dichloromethane. The excitation wavelength for **9d** was 610 nm.

naphthalene diimide **8b**, for the diaminosubstituted NDIs **9a** and **9b** bearing one or two arylamino substituents at the naphthalene core the S_0-S_1 band is not well structured and they do not exhibit any fluorescence.

In contrast to the distinct effect of alkyl- versus arylamino substituents at the naphthalene core on the optical properties of NDIs, few changes in absorption and emission properties were noted for NDIs containing different substituents at the imide positions. Thus, compounds **8a**,**c** and **14a** show very similar absorption and fluorescence spectra and quantum yields (Table 1), despite the fact that they bear different types of substituents (alkyl, aryl, or hydrogen) at the imide positions.

Both series of dyes (red, **8a**,**c**, **13a**, **14a**; blue, **9a**−**e**, **13b**, **14b**) exhibit a second absorption band between 320 and 370 nm which can be attributed to the electronic S_0-S_2 transition. With its strongly pronounced vibronic fine structure with an energy order of ca. 1300 cm^{-1} (0.16 eV), this band strongly resembles the S_0-S_1 band of core-unsubstituted NDIs **1**.

As mentioned above and shown in Table 1, alkylamino- and arylamino-functionalized NDI dyes possess quite different optical properties. NMR studies and molecular modeling provide a reasonable explanation for the observed differences. ^{1}H NMR spectra of alkylamino- and arylamino-substituted NDI show a sharp signal for the amino proton at 9 to 11 ppm, even in highly polar solvents such as DMSO, which clearly suggests that both of these chromophore systems are rigidified by strong intramolecular hydrogen bonding between the amino proton and the adjacent carbonyl group. As a consequence of this intramolecular hydrogen bonding, the amino groups at the naphthalene core are arranged in such a way that the nitrogen lone pair can fully conjugate to the electron-poor naphthalene diimide core in both alkylamino- and arylamino-functionalized NDIs (Figure 4).[16] This affords donor−acceptor chromophores with similar absorption maxima for both alkylamino and arylamino derivatives as well as strong solvatochromic properties as discussed in detail in our earlier work.[7] A further consequence of the hydrogen bonding is that in the case of the arylamino-substituted compounds, the fixed conformation provokes sterical hindrance between the naphthalene core and the aryl substituent. Indeed, molecular modeling studies revealed a pronounced distortion of the aryl substituent relative to the molecule plane. Such a twisted conformation is prone to vibrational degrees of freedom ("librations") leading to a loss of the vibronic fine structure of absorption spectra. Furthermore, new channels for radiationless deactivation of excited states such as twisted internal charge transfer (TICT) process[17] and so-called loose-bolt mechanism[18] may emanate from such twisted geometry which might be responsible for the luminescence quenching of arylamino-substituted NDIs **8b**, **9a**, and **9b** (Table 1).

Redox Properties. Our detailed investigations of the optical properties of these NDIs (vide supra) have shown that substituents at the naphthalene core have dramatic effect on the electronic properties of these dyes. Further insight into the influence of core substituents on the electronic properties of NDIs was gained by cyclic voltammetry which was carried out for a selection of NDIs bearing different substitution patterns at the naphthalene core. The results are summarized in Table 2. The cyclic voltammograms of compounds **7a**, **1a**, and **8a** bearing *n*-octylamine substituents at the imide positions showed two reversible reduction waves (Figure 5), implying the formation of radical anions and dianions, but no reversible oxidation of these compounds could be observed up to 1.2 V vs Fc/Fc^+ (Fc: ferrocene). Within this series, the dichloro-substituted

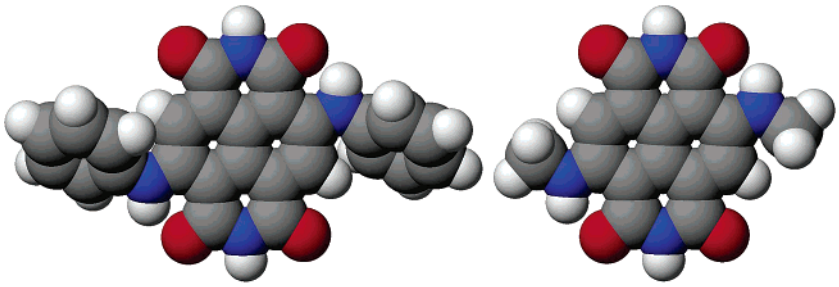


FIGURE 4. Energy-minimized structures of a 2,6-diarylamino-substituted (left) and a 2,6-dialkylamino-substituted (right) NDI obtained from semiempirical calculations (AM1).[16]

TABLE 2. Redox Properties of Alkylamino- (7a, 1a, 8a, and 9d) and Arylamino-Substituted (8b, 9a, and 9b) NDIs Bearing Different Patterns of Donor and Acceptor Substituents at the Naphthalene Core[a]

	$E_{1/2}$ (V vs Fc/Fc^+)			
	X^-/X^{2-}	X/X^-	X/X^+	X^+/X^{2+}
7a	−1.38	−0.95	*b*	*b*
1a	−1.51	−1.10	*b*	*b*
8a	−1.64	−1.24	*b*	*b*
9d	−1.80	−1.40	0.60	*b*
8b	−1.57	−1.21	1.03	*b*
9a	−1.74	−1.41	0.62	1.06
9b	−1.68	−1.38	0.64	1.03

[a] All measurements were conducted in dichloromethane; scan rate 100 mV s^{-1}, concentration 1.0 mM, supporting electrolyte: tetrabutylammonium hexafluorophosphate (NBu_4PF_6, 100 mM). [b] Not observed.

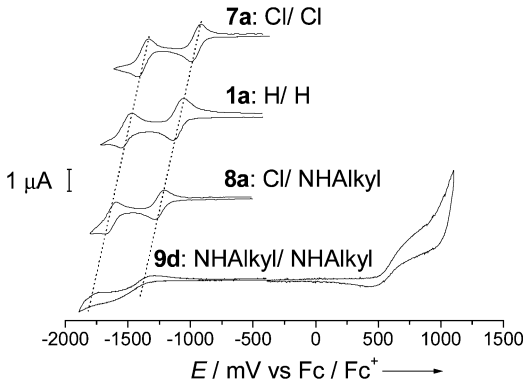


FIGURE 5. Cyclic voltammograms of alkylamino-substituted NDIs **7a**, **1a**, **8a**, and **9d**.

compound **7a** exhibited the most positive reduction potentials of −0.95 and −1.38 V. A gradual shift of the reduction potentials to more negative values was observed for the core-unsubstituted compound **1a** (−1.51 and −1.10 V) and the monochloromonoalkylamino derivative **8a** (−1.64 and −1.24 V) revealing a direct relationship between the electron-donating properties of the core substituents and the electrochemical properties of NDIs. Indeed, for the most electron-rich dialkylamino-substituted naphthalene diimide **9d** significantly lower reduction potentials (−1.80 and −1.40 V) were observed, and the reductions are irreversible. An additional irreversible oxidation wave was observed for **9d** at around +0.6 V vs Fc/Fc^+ (Figure 5). It is noteworthy that at higher scan speeds no quasireversible behavior was observed for **9d**, which suggests that the charged species of this compound is of lower stability compared with those of other naphthalene diimides studied here.

For comparison, the redox properties of arylamino-substituted NDIs **8b**, **9a**, and **9b** have been studied. The redox potentials of these compounds are given in Table 2, and the cyclic voltammograms are shown in Figure 6. The monochloromonoarylamino NDI **8b** showed reduction potentials at −1.57 and −1.21 V that are in the same range as observed for its alkylamino-substituted counterpart **8a** (−1.64 and −1.24 V) (Table 2). However, in contrast to **8a**, for NDI **8b** a reversible oxidation potential was observed at 1.03 V. Analogously, the

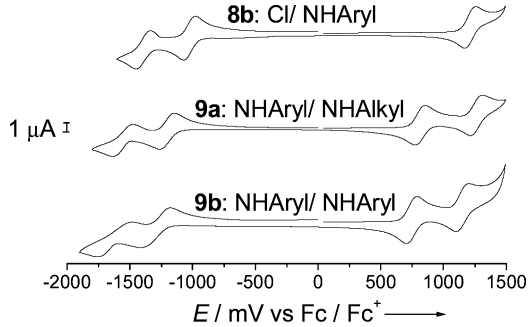


FIGURE 6. Cyclic voltammograms of arylamino-substituted NDIs **8b**, **9a**, and **9b**.

monoarylamino-monoalkylamino derivative **9a** and the diarylamino derivative **9b** showed similar reduction potentials as their dialkylamino counterpart **9d**. But, in contrast to the irreversible oxidation of the latter, both **9a** (0.62 and 1.06 V) and **9b** (0.64 and 1.03 V) display two reversible oxidations, implying an increase in stability of the radical cationic and the dicationic species of arylamino-substituted NDIs compared to those of alkylamino-substituted derivatives.

Conclusion

Selective and stepwise nucleophilic substitution of 2,6-dichloronaphthalene dianhydride **6** with alkyl- and arylamines provided a series of intensely colored red and blue NDI chromophores. With this series of differently core-substituted NDIs, a structure−property relationship could be explored for this class of dyes. Our studies have shown that alkylamino groups with strong electron-donating properties strongly enhance the fluorescence, while arylamino groups diminish fluorescence. The redox properties of NDIs are also influenced by core substituents. As the dichloro-substituted NDI **7a** possesses a low reduction potential, it is a promising candidate for *n*-type organic semiconducting materials which are still very rare.[19] In contrast, substituents at the imide positions do not have any significant effect on the chromophore properties.

Experimental Section

1,2,3,5,6,7,8,10-Octachloro-1,2,6,7-tetrahydropyrene (3). In a 2-L three-necked flask equipped with a mechanical stirrer, a gas inlet tube, and an outlet tube pyrene (100 g, 0.494 mol) and iodine (3.0 g) were dissolved in 1,2,4-trichlorobenzene (1 L) to result in a violet solution. Chlorine gas was then bubbled through the solution constantly. After 45 min, the flask was heated to 50 °C by an oil bath and the formation of a light green solid was observed. After an additional 45 min, the temperature was increased to 110 °C, and after 2.5 h at this temperature, the solid dissolved again. After an additional 2 h, addition of chlorine was stopped, the heating was turned off, and the reaction mixture was cooled to room temperature gradually. A white solid precipitated, which was separated by filtration, washed with toluene (2 × 200 mL), and dried in vacuo. Yield: 89.0 g (38%). Mp: 290 °C. MS (EI) *m*/*z*: 481.9 (13) [M^+] (calcd 481.9). Anal. Calcd for $C_{16}H_6Cl_8$: C, 39.88; H, 1.26. Found: C, 40.03; H, 1.50. Due to its extremely low

(16) CAChe Work System Pro Version 6.1.12.33, Fujitsu.
(17) Grabowski, Z. R.; Rotkiewicz, K.; Rettig, W. *Chem. Rev.* **2003**, *103*, 3899−4031.
(18) Rademacher, A.; Märkle, S.; Langhals, H. *Chem. Ber.* **1982**, *115*, 2927−2934.
(19) (a) Jones, B. A.; Ahrens, M. J.; Yoon, M.-H.; Facchetti, A.; Marks, T. J.; Wasielewski, M. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6363−6366. (b) Chen, Z.; Debije, M. G.; Debaerdemaeker, T.; Osswald, P.; Würthner, F. *ChemPhysChem* **2004**, *5*, 137−140. (c) Würthner, F.; Schmidt, R. *ChemPhysChem* **2006**, *7*, 793−797.

solubility in common organic solvents, no NMR spectrum could be obtained for **3**.

1,3,5,6,8,10-Hexachloropyrene (4a) and 1,3,5,7,8,10-Hexachloropyrene (4b) Regioisomers. Compound **3** (89.0 g, 0.186 mol) and ethanol (700 mL) were placed in a 3-L three-necked flask equipped with a mechanical stirrer and a condenser. Potassium hydroxide (64.4 g, 1.12 mol) was then added slowly. The suspension was refluxed for 5 h, and the resultant yellow solid was separated by filtration and washed with boiling water (500 mL) to obtain 73.6 g (97%) of an isomeric mixture of **4a**/**4b**. Mp: >350 °C. MS (EI) *m*/*z*: 407.9 (100) [M^+] (calcd 407.9). Anal. Calcd for $C_{16}H_4Cl_6$: C, 47.00; H, 0.99; Cl, 52.02. Found: C, 46.68; H, 1.25; Cl, 52.22. Due to its extremely low solubility in common organic solvents, no NMR spectrum could be obtained for **4a** and **4b**.

2,5,7,10-Tetrachloropyrene-3,8-quinone (5a). In a 100-mL three-necked flask equipped with a thermometer fuming nitric acid (24 mL) was cooled with an ice bath. A portion of the regioisomeric mixture of **4a** and **4b** (8.18 g, 20.0 mmol) was added slowly to maintain the temperature between −5 and +5 °C. The cooled reaction mixture was stirred for a further 15 min. During the reaction, regioisomer **5a** precipitated as orange solid. The precipitate was separated by filtration with a G3 frit and washed with acetic acid (5 × 20 mL) and water (2 × 20 mL). The crude product was purified by sublimation (1 mbar, 240−280 °C) to obtain 3.33 g (45%) of **5a**. Mp: 320−325 °C. MS (EI) *m*/*z*: 369.9 (100) [M^+] (calcd 369.9). ^{1}H NMR (400 MHz, D_2SO_4): δ 7.96 (s, 2H), 6.75 (s, 2H). Anal. Calcd for $C_{16}H_4Cl_4O_2$: C, 51.94; H, 1.09. Found: C, 51.38; H, 1.10.

2,6-Dichloro-1,4,5,8-naphthalenetetracarboxylic Acid Dianhydride (6). In a 100-mL three-necked flask equipped with a thermometer and a condenser, 2.02 g (5.46 mmol) of **5a** were dissolved in concd sulfuric acid (28 mL). The solution was heated with an oil bath at 100 °C under stirring for 10 min. Then fuming nitric acid (3.1 mL) was added slowly by a syringe, whereupon the reaction temperature increased to 130 °C and a yellow solid precipitated. The oil bath was removed, and the reaction mixture was cooled to 70 °C and poured into a portion of ice. The precipitated solid was filtered with a frit (G3) and dried in vacuo. Recrystallization with acetic acid provided 0.908 g (49%) of compound **6**. Mp: >350 °C. MS (EI) *m*/*z*: 336.1 (70) [M^+] (calcd 336.1), 292.0 (100) [$M - CO_2^+$] (calcd 291.9). ^{1}H NMR (400 MHz, THF-d_8): δ 8.79 (s, 2H). Anal. Calcd for $C_{14}H_2Cl_2O_6$: C, 49.89; H, 0.60. Found: C, 49.90; H, 0.68.

General Procedure for the Preparation of 2,6-Dichloro-1,4,5,8-naphthalenetetracarboxylic Acid Diimides 7a,b. To a stirred suspension of 1 equiv of dianhydride **6** in glacial acetic acid (10 mL per mmol dianhydride) was slowly added 4−14 equiv of the respective amine at room temperature. After being heated to reflux for 10 min, the reaction mixture was cooled to room temperature. The resulting colorless to slightly brown precipitate was collected on a Büchner funnel and purified by recrystallization with glacial acetic acid.

***N,N′*-Di-*n*-octyl-2,6-dichloro-1,4,5,8-naphthalenetetracarboxylic Acid Diimide (7a).** Compound **7a** was prepared from **6** (0.51 g, 1.5 mmol) and *n*-octylamine (5.0 mL, 20.5 mmol) according to the general procedure. Yield: 0.59 g (70%). Mp: 240 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.78 (s, 2H), 4.18 (t, J = 7.7 Hz, 4H), 1.74 (m, 4H), 1.5−1.2 (m, 20H), 0.88 (t, J = 6.9 Hz, 6H). UV/vis (CH_2Cl_2): λ_{max}/nm (ϵ/ M^{-1} cm^{-1}) = 400 (13 000), 380 (11 800), 359 (17 200), 252 (55 600). Anal. Calcd for $C_{30}H_{36}Cl_2N_2O_4$: C, 64.40; H, 6.49; N, 5.01. Found: C, 64.15; H, 6.53; N, 4.94.

***N,N′*-Di(4-*tert*-butylphenyl)-2,6-dichloro-1,4,5,8-naphthalenetetracarboxylic Acid Diimide (7b).** Compound **7b** was prepared from **6** (0.17 g, 0.5 mmol) and 4-*tert*-butylaniline (0.32 mL, 2.0 mmol) according to the general procedure. Yield: 0.18 g (60%). Mp: >350 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.85 (s, 2H), 7.60 (d, J = 8.6 Hz, 4H), 7.24 (d, J = 8.6 Hz, 4H), 1.40 (s, 18H). HRMS (ESI, dichloromethane) *m*/*z*: calcd for $C_{34}H_{29}Cl_2N_2O_4$ 599.1504, found 599.1495. Anal. Calcd for $C_{34}H_{28}Cl_2N_2O_4$: C, 68.12; H, 4.71; N, 4.67. Found: C, 67.73; H, 4.86; N, 4.39.

***N,N′*-Di-*n*-octyl-2-chloro-6-*n*-octylamino-1,4,5,8-naphthalenetetracarboxylic Acid Diimide (8a).** A solution of diimide **7a** (0.16 g, 0.28 mmol) and *n*-octylamine (1 mL, 6.0 mmol) in dichloromethane (20 mL) was stirred under exclusion of light at room temperature for 4.5 h. The resulting red solution (intense yellow fluorescence) was poured into a mixture of concd HCl (2 mL) and methanol (70 mL). This mixture was concentrated at room temperature under reduced pressure, and a waxy red solid precipitated, which was isolated by centrifugation and washed with methanol. Yield: 0.18 g (96%). Mp: 197 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 10.05 (t, J = 5.2 Hz, 1H), 8.60 (s, 1H), 8.26 (s, 1H), 4.15 (m, 4H), 3.57 (m, 2H), 1.83 (m, 2H), 1.72 (m, 4H), 1.5−1.2 (m, 30H), 0.89 (m, 9H). HRMS (ESI, THF) *m*/*z*: calcd for $C_{38}H_{55}ClN_3O_4$ 652.3881, found 652.3875. UV/vis (CH_2Cl_2): λ_{max}/nm (ϵ/ M^{-1} cm^{-1}) = 532 (15 300), 504 (11 400, sh), 367 (13 100), 348 (10 700), 331 (8300, sh), 271 nm (43 100). Fluorescence (CH_2Cl_2): λ_{max} = 567 nm. Fluorescence quantum yield: Φ_{fl} = 0.58. Anal. Calcd for $C_{38}H_{54}ClN_3O_4$: C, 69.97; H, 8.34; N, 6.44. Found: C, 69.70; H, 8.36; N, 6.44.

***N,N′*-Di-*n*-octyl-2-chloro-6-(4-*tert*-butylphenylamino)-1,4,5,8-naphthalenetetracarboxylic Acid Diimide (8b).** A suspension of diimide **7a** (0.12 g, 0.2 mmol) and 4-*tert*-butylaniline (0.1 mL, 0.6 mmol) in *N*-ethyldiisopropylamine (3 mL) was stirred under argon for 1 h at 140 °C. The obtained red solution was poured into a mixture of concd HCl (2 mL) and methanol (10 mL). A red solid precipitated which was separated by centrifugation and washed with methanol. Yield: 0.14 g (97%). Mp: 113 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 11.65 (s, 1H), 8.67 (s, 1H), 8.56 (s, 1H), 7.50 (d, J = 6.0 Hz, 2H), 7.28 (d, J = 6.0 Hz, 2H), 4.12 (m, 4H), 1.75 (m, 4H), 1.5−1.2 (m, 20H), 1.38 (s, 9H), 0.87 (m, 6H). HRMS (ESI, THF) *m*/*z*: calcd for $C_{40}H_{51}ClN_3O_4$ 672.3568, found 672.3562. UV/vis (CH_2Cl_2): λ_{max}/nm (ϵ/ M^{-1} cm^{-1}) = 523 (12 900), 369 (11 200), 351 (10 800), 333 (9000), 286 nm (35 000). Anal. Calcd for $C_{40}H_{50}ClN_3O_4$: C, 71.46; H, 7.50; N, 6.25. Found: C, 71.39; H, 7.30; N, 6.13.

***N,N′*-Di(4-*tert*-butylphenyl)-2-chloro-6-*n*-octylamino-1,4,5,8-naphthalenetetracarboxylic Acid Diimide (8c).** A solution of diimide **7b** (30 mg, 0.05 mmol) and *n*-octylamine (0.12 mL, 0.72 mmol) in dichloromethane (4 mL) was stirred for 24 h under exclusion of light at room temperature. The resulting red solution (bright yellow fluorescence) was subjected to column chromatography (dichloromethane/hexane = 2:1, silica gel). Upon concentration under reduced pressure at room temperature, an orange solid precipitated which was separated by centrifugation and washed with hexane. Yield: 30 mg (87%). Mp: 212 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 9.99 (t, J = 5.1 Hz, 1H), 8.70 (s, 1H), 8.36 (s, 1H), 7.59 (m, 4H), 7.25 (m, 4H), 3.54 (m, 2H), 1.75 (m, 2H), 1.5−1.2 (m, 10H), 1.39 (s, 18H), 0.86 (t, J = 7.0 Hz, 3H). HRMS (ESI, THF) *m*/*z*: calcd for $C_{42}H_{47}ClN_3O_4$ 692.3255, found 692.3244. UV/vis (CH_2Cl_2): λ_{max}/nm (ϵ/M^{-1} cm^{-1}) = 534 (16 000), 505 (11 800, sh), 365 (14 400), 348 (13 300), 332 (9200, sh), 270 nm (39 500). Fluorescence (CH_2Cl_2): λ_{max} = 566 nm. Fluorescence quantum yield: Φ_{fl} = 0.58. Anal. Calcd for $C_{42}H_{46}ClN_3O_4$: C, 72.87; H, 6.70; N, 6.07. Found: C, 72.91; H, 6.52; N, 6.12.

***N,N′*-Di-*n*-octyl-2-(4-*tert*-butylphenylamino)-6-*n*-octylamino-1,4,5,8-naphthalenetetracarboxylic Acid Diimide (9a).** A solution of diimide **8b** (30 mg, 0.045 mmol) in *n*-octylamine (3 mL) was stirred under argon at 140 °C for 45 min. After being cooled to room temperature, the resulting blue solution was poured into a mixture of concd HCl (2 mL) and methanol (10 mL). The blue precipitate was separated by centrifugation and washed with methanol. Yield: 20 mg (59%). Mp: 216 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 10.95 (s, 1H), 9.52 (t, J = 5.2 Hz, 1H), 8.55 (s, 1H), 8.17 (s, 1H), 7.49 (d, J = 6.0 Hz, 2H), 7.28 (d, J = 6.0 Hz, 2H), 4.17 (m, 4H), 3.46 (m, 2H), 1.81 (m, 4H), 1.73 (m, 2H), 1.5−1.2 (m, 30H), 1.37 (s, 9H), 0.87 (m, 9H). HRMS (ESI, THF) *m*/*z*: calcd for $C_{48}H_{68}N_4O_4$ 764.5240, found 764.5226. UV/vis

(CH_2Cl_2): λ_{max}/nm (ϵ/M^{-1} cm^{-1}) = 613 (22 200), 575 (13 400, sh), 367 (16 000), 349 (13 600), 286 nm (37 900). Anal. Calcd for $C_{48}H_{68}N_4O_4$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.24; H, 9.06; N, 7.32.

***N,N′*-Di-*n*-octyl-2,6-di(4-*tert*-butylphenylamino)-1,4,5,8-naphthalenetetracarboxylic Acid Diimide (9b).** A suspension of diimide **7a** (50 mg, 0.09 mmol) in 4-*tert*-butylaniline (1 mL) was heated under argon to 180 °C for 1 h. After being cooled to room temperature, the resulting blue solution was poured into a mixture of concd HCl (2 mL) and ethanol (10 mL). The blue precipitate was separated by centrifugation, washed with ethanol, and purified by column chromatography (dichloromethane/hexane = 2:1, silica gel). Yield: 40 mg (57%). Mp: 208 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 11.06 (s, 2H), 8.56 (s, 2H), 7.50 (d, J = 6.0 Hz, 4H), 7.28 (d, J = 6.0 Hz, 4H), 4.16 (m, 4H), 1.72 (m, 4H), 1.5−1.2 (m, 20H), 1.37 (s, 18H), 0.86 (t, J = 6.8 Hz, 6H). HRMS (ESI, THF) *m*/*z*: calcd for $C_{50}H_{64}N_4O_4$ 784.4927, found 784.4920. UV/vis (CH_2Cl_2): λ_{max}/nm (ϵ/M^{-1} cm^{-1}) = 612 (22 800), 369 (15 300), 349 (14 800), 311 nm (39 700). Anal. Calcd for $C_{50}H_{64}N_4O_4$: C, 76.50; H, 8.22; N, 7.14. Found: C, 76.29; H, 8.07; N, 7.10.

***N,N′*-Di(4-*tert*-butylphenyl)-2,6-di-*n*-octylamino-1,4,5,8-naphthalenetetracarboxylic Acid Diimide (9c).** Diimide **7b** (30 mg, 0.05 mmol) was heated under argon in *n*-octylamine (2 mL) at 140 °C for 40 min. After being cooled to room temperature, the resulting blue solution was poured into a mixture of concd HCl (2 mL) and ethanol (10 mL). The blue precipitate was separated by centrifugation and washed with ethanol. Isolation of **9c** from the byproducts of an exchange of the imide substituents, i.e., *N*-(4-*tert*-butylphenyl)-*N′*-(*n*-octyl)diimide and *N,N′*-di-*n*-octyldiimide, was achieved by column chromatography. Yield: 17 mg (43%). Mp: 258 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 9.26 (t, J = 5.2 Hz, 2H), 8.22 (s, 2H), 7.59 (d, J = 8.7 Hz, 4H), 7.25 (d, J = 8.7 Hz, 4H), 3.45 (m, 4H), 1.72 (m, 4H), 1.5−1.2 (m, 20H), 1.40 (s, 18H), 0.86 (t, J = 7.0 Hz, 6H). HRMS (ESI, THF) *m*/*z*: calcd for $C_{50}H_{64}N_4O_4$ 784.4927, found 784.4920. UV/vis (CH_2Cl_2): λ_{max}/nm (ϵ/M^{-1} cm^{-1}) = 618 (23 600), 578 (12 500, sh), 363 (14 100), 346 (12 300), 331 (6300, sh), 283 nm (40 900). Fluorescence (CH_2Cl_2): λ_{max} = 650 nm. Fluorescence quantum yield: Φ_{fl} = 0.55. Anal. Calcd for $C_{50}H_{64}N_4O_4$: C, 76.50; H, 8.22; N, 7.14. Found: C, 76.27; H, 8.12; N, 7.15.

***N,N′*-Di-*n*-octyl-2,6-di-*n*-octylamino-1,4,5,8-naphthalenetetracarboxylic Acid Diimide (9d).** Dianhydride **6** (0.22 g, 0.67 mmol) was heated in *n*-octylamine (3 mL) under argon at 140 °C for 40 min. After being cooled to room temperature, the dark blue solution was poured into a mixture of concd HCl (3 mL) and methanol (50 mL). The blue precipitate was collected on a Büchner funnel and recrystallized from 2-propanol. Yield: 0.35 g (70%). Mp: 205 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 9.33 (t, J = 5.1 Hz, 2H), 8.13 (s, 2H), 4.16 (t, J = 7.8 Hz, 4H), 3.48 (m, 4H), 1.80 (m, 4H), 1.72 (m, 4H), 1.5−1.2 (m, 40H), 0.88 (m, 12H). HRMS (ESI, THF) *m*/*z*: calcd for $C_{46}H_{72}N_4O_4$ 744.5553, found 744.5541. UV/vis (CH_2Cl_2): λ_{max}/nm (ϵ/M^{-1} cm^{-1}) = 575 (12 600, sh), 364 (13 600), 346 (10 800), 331 (6300, sh), 282 nm (46 800). Fluorescence (CH_2Cl_2): λ_{max} = 646 nm. Fluorescence quantum yield: Φ_{fl} = 0.53. Anal. Calcd for $C_{46}H_{72}N_4O_4$: C, 74.15; H, 9.74; N, 7.52. Found: C, 73.92; H, 9.61; N, 7.50.

2,6-Dibromo-1,4,5,8-naphthalenetetracarboxylic Acid Dianhydride (11). A solution of dibromoisocyanuric acid (2.86 g, 10.0 mmol) in oleum (20% SO_3, 50 mL) was added at room temperature to a solution of naphthalene dianhydride **10** (2.68 g, 10.0 mmol) in oleum (20% SO_3, 100 mL) over a period of 4 h. The resulting mixture was stirred at room temperature for 1 h and then cautiously poured onto ice (500 g) to give a bright yellow precipitate. Water (1.5 L) was added, and the mixture was allowed to stand for 3 h. The yellow solid was collected on a Büchner funnel, washed with dilute HCl, and dried. Yield: 3.41 g (80%) of crude product, which was used without further purification. Mp: >350 °C. MS (EI) *m*/*z*: 425.7 (100) [M^+] (calcd 426.0). Anal. Calcd for $C_{14}H_2Br_2O_6$: C, 39.48; H, 0.47. Found: C, 38.90; H, 0.42. Due to its extremely low solubility, no NMR spectrum could be obtained of **11**.

***N,N′*-Di(2-ethylhexyl)-2,6-di(2-ethylhexylamino)-1,4,5,8-naphthalenetetracarboxylic Acid Diimide (9e).** Dianhydride **11** (2.12 g, 5.0 mmol) was heated in 2-ethylhexylamine (15 mL) under argon at 140 °C for 2 h. The resulting dark blue solution was cooled to room temperature and poured into a mixture of concd HCl (10 mL) and methanol (100 mL). The blue precipitate was collected on a Büchner funnel and washed with methanol. Purification was achieved by column chromatography (dichloromethane/hexane = 2:1, silica gel). Yield: 1.67 g (45%). Mp: 146 °C. ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ 9.40 (t, J = 5.3 Hz, 2H), 8.10 (s, 2H), 4.11 (d, 4H), 3.40 (m, 4H), 1.93 (m, 2H), 1.72 (m, 2H), 1.5−1.2 (m, 32H), 0.89 (m, 24H). HRMS (ESI, THF) *m*/*z*: $C_{46}H_{72}N_4O_4$ 744.5553, found 744.5547. UV/vis (CH_2Cl_2): λ_{max}/nm (ϵ/M^{-1} cm^{-1}) = 619 (22 100), 576 (11 600, sh), 365 (12 400), 347 (9700), 330 (4700, sh), 283 nm (44 800). Fluorescence (CH_2Cl_2): λ_{max} = 647 nm. Fluorescence quantum yield: Φ_{fl} = 0.53. Anal. Calcd for $C_{46}H_{72}N_4O_4$: C, 74.15; H, 9.74; N, 7.52. Found: C, 74.12; H, 9.72; N, 7.49.

***N,N′*-Di(2-ethylhexyl)-3,7-di(2-ethylhexylamino)-1-amino-4,5,8-naphthalenetricarboxylic Acid 1,8-Lactam 4,5-Imide (12).** A suspension of **9e** (0.60 g, 0.8 mmol) and KOH (6.73 g, 120 mmol) in a mixture of *tert*-butyl alcohol (60 mL) and water (3 mL) was refluxed for 24 h. After being cooled to room temperature, the red reaction mixture was poured slowly into a stirred aqueous 1 N HCl solution (200 mL). The resulting suspension of an oily violet product was extracted with dichloromethane (2 × 50 mL). The combined extracts were dried with NaCl, concentrated, and subjected to column chromatography (dichloromethane/hexane = 1:1, silica gel). From the concentrated fractions a tarry product was precipitated by addition of methanol. Yield: 0.37 g (64%). Mp: not detected. ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ 9.57 (t, J = 5.5 Hz, 1H), 7.71 (s, 1H), 6.38 (s, 1H), 5.83 (t, J = 5.6 Hz, 1H), 4.10 (m, 2H), 3.73 (m, 2H), 3.32 (m, 4H), 1.92 (m, 2H), 1.71 (m, 2H), 1.5−1.2 (m, 32H), 0.93 (m, 24H). MS (CI) *m*/*z*: 717.5 (100) [M^+] (calcd 717.1). Anal. Calcd for $C_{45}H_{72}N_4O_3$: C, 75.37; H, 10.12; N, 7.81. Found: C, 74.99; H, 10.07; N, 7.71.

Acknowledgment. This work is dedicated to Prof. Manfred Christl on the occasion of his 65th birthday. We thank Prof. P. Bäuerle, Prof. U. Nienhaus, Dr. E. Mena-Osteritz, and Dr. Götz (all Universität Ulm) for helpful discussions, in particular, with regard to the photoluminescence and cyclic voltammetry investigations. C.R. is grateful to the Degussa Stiftung for a Ph.D. scholarship. Financial support of our work by the Fonds der Chemischen Industrie is greatly appreciated.

Supporting Information Available: General experimental methods. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0612269